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On the use of the quasi-Gaussian entropy theory in noncanonical ensembles. II. Prediction of density dependence of thermodynamic properties

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In previous articles we derived and tested the quasi-Gaussian entropy theory, a description of the excess free energy in terms of the potential or full internal energy or enthalpy probability distribution, instead of the (configurational) partition function. We obtained in this way the temperature dependence of thermodynamic functions in the *NVT*, *NpT* and μVT ensembles assuming a Gaussian, Gamma or Inverse Gaussian distribution. In this article we extend the theory to describe the density dependence of thermodynamic properties, using the distribution of volume and number of particles in the isothermal-isobaric and grand canonical ensemble, respectively. In both ensembles pressure-density expressions for a Gaussian and various Gamma distributions are derived and applied to water. A Gamma description for the volume distribution turns out to be a good model in the gas range, which is in accordance with the volume distribution of an ideal gas. A Gamma description for the particle number distribution works well for liquid densities. © *1998 American Institute of Physics.* [S0021-9606(98)50332-7]

I. INTRODUCTION

The prediction of the temperature and density behavior of realistic fluidlike molecular systems based on an exact statistical mechanical approach is both very challenging and important for practical applications and the prediction of equations of state. The evaluation of the partition function for systems with interacting molecules is in general extremely difficult, and often severe approximations have to be made, unlike the situation for molecules in the ideal gas phase, see for example Frenkel *et al.*[1]

However, as we have shown in previous articles,[2–7] for the evaluation of macroscopic thermodynamic properties of realistic systems most of the information which is present in the partition function is redundant. It is sufficient to focus on the probability distribution of the appropriate fluctuations in the system, which completely determine the free energy difference with respect to a proper reference. This is the approach of the quasi-Gaussian entropy theory (QGE). Its basic principles are explained in Sec. II of the preceding article.[7] In that article we derived the temperature dependence of thermodynamic properties in various ensembles.

In the present paper we will describe how to extend the quasi-Gaussian entropy theory in an exact way to describe the density dependence of thermodynamic functions in the isothermal-isobaric and grand canonical ensemble. This is accomplished by using distributions of the volume and number of particles. Just as for the temperature dependence in the previous article,[7] we can immediately obtain expressions for the thermodynamic functions without explicitly solving the appropriate thermodynamic master equation (TME).

The article is organized as follows.

In Sec. II we present the theory concerning density dependence of thermodynamic properties using the QGE approach. The definition of the system and reference state (Sec. II A), a discussion on the distribution of the volume and number of particles (Sec. II B), the derivation of related thermodynamic functions from the free energy (Sec. II C) and some important model distributions (Gaussian and Gamma) and corresponding statistical states (Sec. II D) are described. As the isothermal-isobaric and the grand canonical ensemble differ in some important aspects, the specific applications and ''special'' statistical states of these ensembles are discussed in Secs. II E and II F. To facilitate the derivations, we use a unified notation for properties in various ensembles as introduced before,[7] see Table I.

A discussion on the thermodynamic master equation and its implications for phase transitions is presented in Sec. III. Applications to water of the various statistical states are presented in Sec. IV, along with some results on a model system, the ideal gas. Finally, in Sec. V we give the conclusions.

II. THEORY

A. Definition of the system and reference state

The density dependence of thermodynamic properties, i.e., the dependence on volume (isothermal-isobaric ensemble) or particle number (grand canonical ensemble), can be obtained in the following way.

In the *isothermal-isobaric ensemble* the Gibbs free energy difference between two different pressures is

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TABLE I. Notation of different properties in various ensembles, where in general x, y, and z are the independent variables, λ is the appropriate label, F, W, S and C are the thermodynamic potential (free energy), heat function, entropy and heat capacity, Y and Z are ''conjugated'' properties and Υ is the partition function. $J=-pV$ is the grand potential and $D=U-\mu N$ the corresponding heat function. For completeness we also included the canonical ensemble.

Ensemble	x	y	z	λ	F	W	S	C	$Y=\left(\frac{\partial F}{\partial y}\right)_{T,z}$	$Z=\left(\frac{\partial F}{\partial z}\right)_{T,y}$	Υ
Isothermal-isobaric	T	p	N	p	G	H	S	C_p	V	μ	Δ
Grand canonical	T	μ	V	μ	J	D	S	C_μ	$-N$	$-p$	Ξ
Canonical	T	V	N	V	A	U	S	C_V	$-p$	μ	Q

$$\begin{aligned}\Delta G &= G(p)-G(p^0)\\ &= -kT\ \ln\frac{\int_0^\infty d\mathscr{V}\, e^{-\beta p\mathscr{V}}Q(N,\mathscr{V},T)}{\int_0^\infty d\mathscr{V}\, e^{-\beta p^0\mathscr{V}}Q(N,\mathscr{V},T)}\\ &= V^0\Delta p - kT\ \ln\langle e^{-\beta\Delta p\Delta\mathscr{V}^0}\rangle_{p^0}\\ &= V^0\Delta p - kT\ \ln\int e^{-\beta\Delta p\Delta\mathscr{V}^0}\rho^0(\Delta\mathscr{V}^0)d\Delta\mathscr{V}^0 \qquad (1)\\ &= V\Delta p + kT\ \ln\langle e^{\beta\Delta p\Delta\mathscr{V}}\rangle\\ &= V\Delta p + kT\ \ln\int e^{\beta\Delta p\Delta\mathscr{V}}\rho(\Delta\mathscr{V})d\Delta\mathscr{V}, \qquad (2)\end{aligned}$$

where $Q(N,V,T)$ is the canonical partition function at constant number of molecules N, volume V and temperature T, and $\int_0^\infty d\mathscr{V}\, e^{-\beta p\mathscr{V}}Q(N,\mathscr{V},T)/v=\Delta(N,p,T)$ is the isothermal-isobaric partition function. As usual we will denote instantaneous extensive properties by calligraphic symbols, whereas the corresponding thermodynamic averages are given in Roman capitals. Furthermore, $\beta=1/kT$, $\Delta p=p-p^0$, $V^0=\langle\mathscr{V}\rangle_{p^0}$, $\Delta\mathscr{V}^0=\mathscr{V}-V^0$, $V=\langle\mathscr{V}\rangle$, $\Delta\mathscr{V}=\mathscr{V}-V$ and $\langle\cdots\rangle_{p^0}$ and $\langle\cdots\rangle$ denote ensemble averages in the p^0 and p ensemble. $\rho^0(\Delta\mathscr{V}^0)$ and $\rho(\Delta\mathscr{V})$ are the distributions of the volume fluctuations at p^0 and p, respectively. Note that the integral on the right-hand side of Eqs. (1) and (2) is only a function of T, N and Δp. Taking the pressure derivative, we obtain

$$\left(\frac{\partial\Delta G}{\partial p}\right)_{T,N}=V(p) \qquad (3)$$

and upon inversion $p(V)$.

In the *grand canonical ensemble* we have in a similar way the grand potential difference ΔJ between two different chemical potentials

$$\Delta J=J(\mu)-J(\mu^0)=-kT\ \ln\frac{\Sigma_{\mathscr{N}=0}^\infty e^{\beta\mu\mathscr{N}}Q(\mathscr{N},V,T)}{\Sigma_{\mathscr{N}=0}^\infty e^{\beta\mu^0\mathscr{N}}Q(\mathscr{N},V,T)}. \qquad (4)$$

There is one major difference between this expression and Eq. (1) $\mathscr{N}$ is a discrete variable and the corresponding distribution of the number of particles is also discrete. However, for a macroscopic system the change due to a single particle can be regarded as a differential. In the case that an analytical expression of $Q(\mathscr{N},V,T)$ is available, we can rewrite the grand canonical partition function as

$$\begin{aligned}\Xi(\mu^0)=e^{-\beta J^0}&=\sum_{\mathscr{N}=0}^\infty e^{\beta\mu^0\mathscr{N}}Q(\mathscr{N},V,T)\\ &\cong 1+\int_0^\infty e^{\beta\mu^0\bar{\mathscr{N}}}Q(\bar{\mathscr{N}},V,T)d\bar{\mathscr{N}} \qquad (5)\end{aligned}$$

by separating the first term (an infinitely deluted system where $\mathscr{N}=0$) and approximating the remaining sum by an integral, where $\bar{\mathscr{N}}$ is a continuous variable and $J^0=J(\mu^0)$. Defining the continuous distribution function at μ^0 as

$$\begin{aligned}\rho^0(\bar{\mathscr{N}})&=\frac{e^{\beta\mu^0\bar{\mathscr{N}}}Q(\bar{\mathscr{N}},V,T)}{\int_0^\infty e^{\beta\mu^0\bar{\mathscr{N}}}Q(\bar{\mathscr{N}},V,T)d\bar{\mathscr{N}}}\\ &=\frac{e^{\beta\mu^0\bar{\mathscr{N}}}Q(\bar{\mathscr{N}},V,T)}{e^{-\beta J^0}-1} \qquad (6)\end{aligned}$$

we have

$$e^{\beta\mu^0\bar{\mathscr{N}}}Q(\bar{\mathscr{N}},V,T)=\rho^0(\bar{\mathscr{N}})(e^{-\beta J^0}-1). \qquad (7)$$

Hence, defining $\Delta\mu=\mu-\mu^0$ we can express Eq. (4) as

$$\begin{aligned}e^{-\beta\Delta J}&=\frac{\Sigma_{\mathscr{N}=0}^\infty e^{\beta\mu\mathscr{N}}Q(\mathscr{N},V,T)}{\Xi(\mu^0)}\\ &=e^{\beta J^0}\left(1+\int_0^\infty e^{\beta\Delta\mu\bar{\mathscr{N}}}e^{\beta\mu^0\bar{\mathscr{N}}}Q(\bar{\mathscr{N}},V,T)d\bar{\mathscr{N}}\right)\\ &=e^{\beta J^0}+(1-e^{\beta J^0})\int_0^\infty e^{\beta\Delta\mu\bar{\mathscr{N}}}\rho^0(\bar{\mathscr{N}})d\bar{\mathscr{N}}, \qquad (8)\end{aligned}$$

where in the last step we have used Eq. (7). For macroscopic systems, not at extremely low pressure and density, $e^{\beta J^0}\approx 0$ (even for a system of 1 μm^3 at 0.1 Pa and 300 K we find $e^{\beta J^0}\sim 3\cdot 10^{-11}$). Hence under normal conditions we can safely neglect the first term on the right-hand side of Eq. (5).

$$\Xi(\mu^0)=e^{-\beta J^0}=\int_0^\infty e^{\beta\mu^0\bar{\mathscr{N}}}Q(\bar{\mathscr{N}},V,T)d\bar{\mathscr{N}} \qquad (9)$$

and from Eq. (8) simply follows

$$\Delta J = -N^0\Delta\mu - kT\ \ln\langle e^{\beta\Delta\mu\Delta\overline{\mathscr{N}}^0}\rangle_{\mu^0}$$
$$= -N^0\Delta\mu - kT\ \ln\int e^{\beta\Delta\mu\Delta\overline{\mathscr{N}}^0}\rho^0(\Delta\overline{\mathscr{N}}^0)d\Delta\overline{\mathscr{N}}^0 \tag{10}$$

$$= -N\Delta\mu + kT\ \ln\langle e^{-\beta\Delta\mu\Delta\overline{\mathscr{N}}}\rangle$$
$$= -N\Delta\mu + kT\ \ln\int e^{-\beta\Delta\mu\Delta\overline{\mathscr{N}}}\rho(\Delta\overline{\mathscr{N}})d\Delta\overline{\mathscr{N}} \tag{11}$$

with $N^0=\langle\overline{\mathscr{N}}\rangle_{\mu^0}$, $\Delta\overline{\mathscr{N}}^0=\overline{\mathscr{N}}-N^0$, $N=\langle\overline{\mathscr{N}}\rangle$ and $\Delta\overline{\mathscr{N}}=\overline{\mathscr{N}}-N$. $\langle\cdots\rangle_{\mu^0}$ and $\langle\cdots\rangle$ denote ensemble averages in the μ^0 and μ ensemble and $\rho^0(\Delta\overline{\mathscr{N}}^0)$ and $\rho(\Delta\overline{\mathscr{N}})$ are the continuous distributions of the particle number fluctuations at μ^0 and μ, respectively. In this paper we will use these virtually exact equations. Only in the limit of zero pressure or density when $\Delta\mu$ really tends to $-\infty$ Eq. (8) has to be used, see Sec. II F. It is important to note that Eq. (9) implies the equality between the moments of the continuous number of particles, $\overline{\mathscr{N}}$, and the ones of the discrete number, $\mathscr{N}$. Hence for systems not in the zero pressure limit, we can really consider the instantaneous number of particles as the continuous variable $\overline{\mathscr{N}}$.

The integral on the right-hand side of Eqs. (10) and (11) is only depending on T, V and $\Delta\mu$. Taking the derivative with respect to the chemical potential yields

$$\left(\frac{\partial\Delta J}{\partial\mu}\right)_{T,V} = -N(\mu) \tag{12}$$

and upon inversion $\mu(N)$.

Hence adopting the general symbols as defined in Table I and defining $\Delta y=y-y^0$, $Y^0=\langle\mathscr{Y}\rangle_{y^0}$, $\Delta\mathscr{Y}^0=\mathscr{Y}-Y^0$ with $\mathscr{Y}$ the instantaneous Y and $\rho^0(\Delta\mathscr{Y}^0)$ the probability distribution of $\Delta\mathscr{Y}^0$ at y^0, we have using the y^0 ensemble from Eqs. (1) and (10),

$$\Delta F = F(y)-F(y^0)$$
$$= Y^0\Delta y - kT\ \ln\langle e^{-\beta\Delta y\Delta\mathscr{Y}^0}\rangle_{y^0}$$
$$= Y^0\Delta y - kT\ \ln\int e^{-\beta\Delta y\Delta\mathscr{Y}^0}\rho^0(\Delta\mathscr{Y}^0)d\Delta\mathscr{Y}^0, \tag{13}$$

$$\left(\frac{\partial\Delta F}{\partial y}\right)_{T,z} = Y(y), \tag{14}$$

and upon inversion $y(Y)$. Note that we use a zero *super* script to denote that the property is evaluated at y^0, in order to distinguish this from the zero *sub*script as used in the preceding article,[7] meaning ''evaluated at the reference temperature T_0.'' The expression $\langle e^{-\beta\Delta y\Delta\mathscr{Y}^0}\rangle_{y^0} \equiv G^0_{\Delta\mathscr{Y}^0}(-\beta\Delta y)$ is actually the *central moment generating function*[8,9] (MGF) of the probability distribution $\rho^0(\Delta\mathscr{Y}^0)$, and its natural logarithm is called the *cumulant generating function* (CGF). In general, for a distribution $\rho(\xi)$ the central MGF is $G_{\Delta\xi}(t)=\langle e^{t\Delta\xi}\rangle$ with $\Delta\xi=\xi-\langle\xi\rangle$ and the MGF is $G_{\xi}(t)=\langle e^{t\xi}\rangle$. Equation (13) shows that the excess free energy is completely determined by the volume or particle number distribution via the MGF or CGF.

As mentioned in the previous paper,[7] an expression of the type of Eq. (13), $\Delta F=-kT\ \ln\langle e^{-\beta\Delta y\mathscr{Y}}\rangle_{y^0}$, is often expanded in powers of $-\beta\Delta y$ and truncated after the second, third or fourth order term, a so-called cumulant expansion. This has been done mostly for the temperature dependence of thermodynamic properties, especially in combination with molecular dynamics or Monte Carlo simulations.[10–16] In this paper we will not use a truncated cumulant expansion, but focus on the use of physically acceptable (model) distributions for ρ^0.

B. Volume and particle number distribution

We can use the central limit theorem to show that for macroscopic systems, which may be considered as a very large collection of identical independent subsystems, $\rho^0(\Delta\mathscr{Y}^0)$ can be described by a unimodal distribution close to a Gaussian. Since it is statistical mechanically defined as

$$\rho^0(\Delta\mathscr{Y}^0) = \frac{Q(\Delta\mathscr{Y}^0+Y^0)e^{-\beta y^0(\Delta\mathscr{Y}^0+Y^0)}}{\Upsilon^0} \tag{15}$$

it follows that

$$\frac{d\rho^0}{d\Delta\mathscr{Y}^0} = -\rho^0\left[\beta y^0 - \frac{\partial\ \ln\ Q(\Delta\mathscr{Y}^0+Y^0)}{\partial\Delta\mathscr{Y}^0}\right]$$
$$= -\rho^0\ \frac{(\Delta\mathscr{Y}^0-\Delta\mathscr{Y}^0{}_m)P^m(\Delta\mathscr{Y}^0)}{G^n(\Delta\mathscr{Y}^0)} \tag{16}$$

by expanding the expression between square brackets in a Padé approximant[17,18] around the mode (maximum of probability) of the distribution. In Eq. (16) $P^m(\Delta\mathscr{Y}^0)=\Sigma_{i=0}^m a_i^0(\Delta\mathscr{Y}^0)^i$ and $G^n(\Delta\mathscr{Y}^0)=\Sigma_{j=0}^n b_j^0(\Delta\mathscr{Y}^0)^j$ are arbitrary polynomials in $\Delta\mathscr{Y}^0$, and $\Delta\mathscr{Y}^0{}_m$ is the position of the mode. Equation (16) represents the generalized Pearson system. Via the method of moments[19] the parameters $\{a_i^0\}$ and $\{b_j^0\}$ can be related to the central moments of $\mathscr{Y}$ evaluated at y^0, i.e. $M_k^0=M_k^0[\mathscr{Y}]=\langle(\Delta\mathscr{Y}^0)^k\rangle_{y^0}$, which via statistical mechanics,[20,21] can be expressed in terms of derivatives of Y in y at y^0:

$$M_2^0 = (-kT)\left(\frac{\partial Y^0}{\partial y}\right)_{T,z},$$
$$M_3^0 = (-kT)^2\left(\frac{\partial^2 Y^0}{\partial y^2}\right)_{T,z}, \tag{17}$$
$$\cdots,$$

where $(\partial^k Y^0/\partial y^k)_{T,z}$ denotes $(\partial^k Y/\partial y^k)_{T,z}$ evaluated at y^0. Note that $M_{2k+1}^0[-\mathscr{Y}]=-M_{2k+1}^0[\mathscr{Y}]$, so in the grand canonical ensemble we have for example $M_3^0[\mathscr{Y}]=-M_3^0[\overline{\mathscr{N}}]$. Depending on the complexity of the distribution ρ^0, ΔF and hence $Y(y)$ can be expressed in terms of a limited set of parameters $\{Y^0,\partial Y^0/\partial y,\ldots,\partial^{r-1}Y^0/\partial y^{r-1}\}$ if M_r^0 is the highest order moment that is required to define all parameters. Each type of distribution again defines a different statistical state of the system. Moreover, we can formu-

late restrictions on the solutions of Eq. (16), such as the distribution being unimodal (see also Ref. 2). Additional restrictions for the two specific ensembles are formulated in Secs. II E and II F.

C. Derivation of conjugated properties

It should be also noted that since the parameters $Y^0, \partial Y^0/\partial y, \ldots, \partial^{r-1}Y^0/\partial y^{r-1}$ are implicitly functions of T and z, just like in the previous article[7] on the temperature dependence we can obtain further thermodynamic properties from Eqs. (13) and (14) via

$$-S=\left(\frac{\partial F}{\partial T}\right)_{y,z}=\frac{\partial F}{\partial F^0}\left(\frac{\partial F^0}{\partial T}\right)_{y,z}+\sum_{l=0}^{r-1}\frac{\partial F}{\partial f^{l,0}}\left(\frac{\partial f^{l,0}}{\partial T}\right)_{y,z}, \tag{18}$$

where we have defined

$$f^{0,0}=Y^0; \quad f^{l,0}=\left(\frac{\partial^l Y^0}{\partial y^l}\right)_{T,z}. \tag{19}$$

Using

$$\left(\frac{\partial F^0}{\partial T}\right)_{y,z}=-S^0 \tag{20}$$

and the Maxwell relations

$$\left(\frac{\partial f^{0,0}}{\partial T}\right)_{y,z}=\left(\frac{\partial Y^0}{\partial T}\right)_{y,z}=-\left(\frac{\partial S^0}{\partial y}\right)_{T,z}, \tag{21}$$

$$\left(\frac{\partial f^{l,0}}{\partial T}\right)_{y,z}=\left(\frac{\partial}{\partial T}\left(\frac{\partial^l Y^0}{\partial y^l}\right)_{T,z}\right)_{y,z}=-\left(\frac{\partial^{l+1}S^0}{\partial y^{l+1}}\right)_{T,z}, \tag{22}$$

we obtain

$$S(y)=S^0+\sum_{l=0}^{r-1}\frac{\partial F}{\partial f^{l,0}}\left(\frac{\partial^{l+1}S^0}{\partial y^{l+1}}\right)_{T,z}. \tag{23}$$

D. Statistical states

In the following we will describe the solutions of $\Delta F, Y(y)$ and hence $y(Y)$ for the Gaussian and Gamma state with the help of Eqs. (13)–(14). In the two subsequent sections we will derive for the isothermal-isobaric and grand canonical ensemble specific Gamma states, according to the specific physical restrictions valid for each ensemble. Unlike for the analogous case in the temperature,[7] in this paper we will not explicitly describe the solutions of the conjugated equations [Eqs. (18)–(22)] for these statistical states.

For a *Gaussian state*, defined by the Gaussian distribution[2,6]

$$\rho(\Delta\xi)=\frac{1}{\sqrt{2\pi b_0}}\exp\left\{-\frac{(\Delta\xi)^2}{2b_0}\right\} \tag{24}$$

for the variable $\Delta\xi=\xi-\langle\xi\rangle$, the cumulant generating function is

$$\ln G_{\Delta\xi}(t)=\ln\langle e^{t\Delta\xi}\rangle=\tfrac{1}{2}b_0t^2 \tag{25}$$

with $b_0=M_2$. In this case, with $t=-\beta\Delta y$, $\Delta\xi=\Delta\mathscr{Y}^0$, $b_0=b_0^0=M_2^0$ and M_2^0 given by Eq. (17) we obtain

$$\Delta F=Y^0\Delta y+\frac{1}{2}\left(\frac{\partial Y^0}{\partial y}\right)_{T,z}\Delta y^2, \tag{26}$$

$$Y(y)=Y^0+\left(\frac{\partial Y^0}{\partial y}\right)_{T,z}\Delta y, \tag{27}$$

$$y(Y)=y^0+\left(\frac{\partial y}{\partial Y^0}\right)_{T,z}(Y-Y^0). \tag{28}$$

Clearly, $y(Y)$ is equal to a first order Taylor expansion of y in Y around Y^0, or equivalently a [1/0] Padé approximant[18,22] of y around Y^0. Note that, because of the special properties of the Gaussian distribution, the Gaussian state is equivalent to a second order cumulant expansion.

For a *Gamma state*, defined by the Gamma distribution[2,6]

$$\rho(\Delta\xi)=\frac{b_1(1/b_1^2)^{b_0/b_1^2}}{\Gamma(b_0/b_1^2)}(b_0+b_1\Delta\xi)^{b_0/b_1^2-1}\times\exp\left\{-\frac{b_0+b_1\Delta\xi}{b_1^2}\right\} \tag{29}$$

with $\Gamma(\cdot)$ the Gamma function,[23] the cumulant generating function is

$$\ln G_{\Delta\xi}(t)=\ln\langle e^{t\Delta\xi}\rangle=-b_0\left[\frac{1}{b_1}t+\frac{1}{b_1^2}\ln(1-b_1t)\right] \tag{30}$$

with $b_0=M_2$ and $b_1=M_3/2M_2$. In this case, with $t=-\beta\Delta y$, $\Delta\xi=\Delta\mathscr{Y}^0$, $b_0=b_0^0=M_2^0$, $b_1=b_1^0=M_3^0/2M_2^0$ and M_2^0 and M_3^0 given by Eq. (17) we find

$$\Delta F=Y^0\Delta y+\left(\frac{\partial Y^0}{\partial y}\right)_{T,z}\left[\frac{1}{\theta^0}\Delta y-\frac{1}{(\theta^0)^2}\ln(1+\theta^0\Delta y)\right], \tag{31}$$

$$Y(y)=Y^0+\left(\frac{\partial Y^0}{\partial y}\right)_{T,z}\frac{\Delta y}{1+\theta^0\Delta y}, \tag{32}$$

$$y(Y)=y^0+\frac{Y-Y^0}{(\partial Y^0/\partial y)_{T,z}-\theta^0(Y-Y^0)}, \tag{33}$$

where we have defined

$$\theta^0=\frac{b_1^0}{kT}=\frac{M_3^0}{2kTM_2^0}=-\frac{(\partial^2Y^0/\partial y^2)_{T,z}}{2(\partial Y^0/\partial y)_{T,z}}. \tag{34}$$

In this case the function $y(Y)$ is equal to a [1/1] Padé approximant of y around Y^0. Note that the Gaussian state equations follow directly from the Gamma state ones using the limit $\theta^0\to 0$.

E. Isothermal-isobaric ensemble

At this point it is useful to address some specific features of the isothermal-isobaric ensemble and the corresponding restrictions on the possible solutions of the generalized Pearson system.

Clearly, for $p=0$ (i.e., $y=0$) the Gibbs free energy ΔG diverges, see Eq. (1), as $\int_0^\infty \exp\{-\beta A(\mathscr{V})\}d\mathscr{V}\to\infty$ since A is a decreasing function of V because $\partial A/\partial V=-p<0$. Therefore the distribution ρ^0 must have a MGF $\langle e^{t\xi}\rangle$ which

diverges at one finite value of t, and since the volume distributions are defined from a finite lower limit $V_{\min}$ to infinity, we must select solutions of the generalized Pearson system with $m+1=n$ [cf. Eq. (16) and Ref. 7] and

$$1/b_n^0 = t_d = \lim_{p\to 0} -\beta\Delta p = \beta p^0 \tag{35}$$

eliminating in this way one parameter and reducing the complexity of the solution.

For a *diverging Gamma state*, which is the first completely acceptable statistical state in this ensemble, we use Eq. (35), yielding $\beta b_1^0 = \theta^0 = 1/p^0$. Combining this with the previous expressions for a general Gamma state, Eqs. (31)–(34) we obtain

$$\Delta G = V^0\Delta p + p^0\left(\frac{\partial V^0}{\partial p}\right)_{T,N}\left[\Delta p - p^0\,\ln\left(\frac{p}{p^0}\right)\right], \tag{36}$$

$$V(p) = V^0 + p^0\left(\frac{\partial V^0}{\partial p}\right)_{T,N}\left[1-\frac{p^0}{p}\right], \tag{37}$$

$$p(V) = -\frac{{p^0}^2(\partial V^0/\partial p)_{T,N}}{V-V_{\min}}, \tag{38}$$

with

$$V_{\min} = V^0 + p^0\left(\frac{\partial V^0}{\partial p}\right)_{T,N}, \tag{39}$$

where the function $p(V)$ is equal to a [0/1] Padé approximant of p around V^0 and $V_{\min}<V^0$ since for reasons of thermodynamic stability $(\partial V^0/\partial p)_{T,N}<0$.

In the isothermal-isobaric ensemble the limit to the point of divergence of the MGF, $p\to 0$, corresponds to $V\to\infty$ and clearly to an ideal gas condition. This implies that the proper description of any gas phase (or fluid phase above the critical point) must be a diverging state. Since from Eq. (37) it follows that the expression $p^2(\partial V/\partial p) = {p^0}^2(\partial V^0/\partial p)$ is volume independent, and the input parameters can be obtained at arbitrary V^0, the value of $p^2(\partial V/\partial p)$ can also be calculated in the ideal gas condition, giving

$${p^0}^2\left(\frac{\partial V^0}{\partial p}\right)_{T,N} = -NkT, \tag{40}$$

whence from Eqs. (38) and (39) we obtain the very simple equations

$$p(V) = \frac{NkT}{V-V_{\min}}, \tag{41}$$

$$V_{\min} = V^0 - \frac{NkT}{p^0}. \tag{42}$$

Clearly, Eq. (41) resembles a van der Waals like expression of the pressure, although derived in a completely different way. $V_{\min}$ is the ''minimum'' volume of the system, which must be zero or positive and temperature independent for a system described by an exact diverging Gamma state, like in the van der Waals equation, where $V_{\min}=(2/3)\pi N\sigma_{\mathrm{HS}}^3$ (Ref. 24) can be identified as the hard sphere volume of the molecules. When the Gamma state is an approximation to a more complex statistical state, $V_{\min}$ extracted from experimental properties reflects the effect of both repulsive (''hard core'') and attractive interactions, in which case $V_{\min}$ is in general temperature dependent and can be even negative (if the attractive forces are dominating, i.e., p^0 is smaller than the ideal gas pressure at V^0). Obviously for an ideal gas $V_{\min}=0$.

For the construction of equations of state, the most useful equations are the $p(V)$ relations. We will therefore summarize the properties of the $p(V)$ equations in the isothermal-isobaric ensemble, i.e., the limits of V and the corresponding pressures.

For a *Gaussian state* $\mathrm{G}[\mathscr{I}]$ for the volume distribution, we have from Eq. (28)

$$p = p^0 + \left(\frac{\partial p}{\partial V^0}\right)_{T,N}(V-V^0) \tag{43}$$

which corresponds to a second order cumulant expansion of ΔG in $\beta\Delta p$. For a *positive Gamma state* $\Gamma_+[\mathscr{I}]$ from Eq. (33)

$$\begin{aligned} p &= p^0 - \frac{V-V^0}{\theta^0(V-V_{\min})},\\ V_{\min} &= V^0 + \frac{1}{\theta^0}\left(\frac{\partial V^0}{\partial p}\right)_{T,N}, \end{aligned} \tag{44}$$

where for a *negative Gamma state* $\Gamma_-[\mathscr{I}]$ we have to interpret $V_{\min}$ as $V_{\max}>V^0$, since in that case both θ^0 and $(\partial V^0/\partial p)$ are negative. Finally, for a *diverging (positive) Gamma state* in the volume, $\Gamma_+^d[\mathscr{I}]$, we have from Eqs. (41) and (42) simply

$$\begin{aligned} p &= \frac{NkT}{V-V_{\min}},\\ V_{\min} &= V^0 - \frac{NkT}{p^0}. \end{aligned} \tag{45}$$

In Table II we have summarized the limit properties of these *NpT* pressure equations. Clearly, of the four expressions the diverging Gamma state is the only completely physically correct solution. A negative Gamma state in the volume is a very unphysical state, even as a local approximation, since both limits are incorrect. The positive Gamma state, however, could be used as a local approximation e.g. at higher density. Note also that a Gaussian state (equivalent to a second order cumulant expansion) is clearly less ''physical'' than the diverging Gamma state, which has even a lower complexity (i.e., number of input data at V^0).

F. Grand canonical ensemble

In this section we will address some specific points of the grand canonical ensemble.

First of all, using standard thermodynamic manipulations, we can rewrite the derivatives $(\partial Y^0/\partial y)_{T,z}$ and $(\partial^2 Y^0/\partial y^2)_{T,z}$, i.e., $(\partial N^0/\partial\mu)_{T,V}$ and $(\partial^2 N^0/\partial\mu^2)_{T,V}$ occurring in Eqs. (26)–(34) in a more convenient form, since $(\partial\mu/\partial N^0)_{T,V} = V(\partial\mu/\partial\rho_N^0)_T$ and

TABLE II. Summary of properties of the $p(V)$ equations in the isothermal-isobaric ensemble, for the Gaussian G[$\mathscr{V}$] [Eq. (43)], positive Gamma $\Gamma_+[\mathscr{V}]$ [Eq. (44)], diverging Gamma $\Gamma_+^d[\mathscr{V}]$ [Eq. (45)] and negative Gamma state $\Gamma_-[\mathscr{V}]$ [Eq. (44)] of the volume distribution $\rho(\mathscr{V})$.

State	θ^0	$V_{\min}$	$\lim_{V\to V_{\min}} p$	$V_{\max}$	$\lim_{V\to V_{\max}} p$
G[$\mathscr{V}$]	0	$-\infty$	∞	∞	$-\infty$
$\Gamma_+[\mathscr{V}]$	>0	$V^0+\left(\frac{\partial V^0}{\partial p}\right)_T \Big/ \theta^0$	∞	∞	p^0-1/θ^0
$\Gamma_+^d[\mathscr{V}]$	$1/p^0$	V^0-NkT/p^0	∞	∞	0
$\Gamma_-[\mathscr{V}]$	<0	$-\infty$	p^0-1/θ^0	$V^0+\left(\frac{\partial V^0}{\partial p}\right)_T \Big/ \theta^0$	$-\infty$

$$\left(\frac{\partial \mu}{\partial \rho_N^0}\right)_T = \frac{1}{\rho_N^0}\left(\frac{\partial p}{\partial \rho_N^0}\right)_T, \tag{46}$$

$$\left(\frac{\partial^2 \mu}{\partial \rho_N^{0\,2}}\right)_T = -\frac{1}{\rho_N^{0\,2}}\left(\frac{\partial p}{\partial \rho_N^0}\right)_T + \frac{1}{\rho_N^0}\left(\frac{\partial^2 p}{\partial \rho_N^{0\,2}}\right)_T, \tag{47}$$

whence

$$\begin{aligned}\theta^0 &= -\frac{M_3^0[\bar{\mathscr{N}}]}{2kTM_2^0[\bar{\mathscr{N}}]} = -\frac{(\partial^2 N^0/\partial \mu^2)_{T,V}}{2(\partial N^0/\partial \mu)_{T,V}} \\ &= -\frac{(\partial^2 \rho_N^0/\partial \mu^2)_T}{2(\partial \rho_N^0/\partial \mu)_T} = \frac{(\partial^2 \mu/\partial \rho_N^{0\,2})_T}{2(\partial \mu/\partial \rho_N^0)_T^2} \\ &= \frac{1}{2(\partial p/\partial \rho_N^0)_T}\left[\frac{\rho_N^0(\partial^2 p/\partial \rho_N^{0\,2})_T}{(\partial p/\partial \rho_N^0)_T} - 1\right],\end{aligned} \tag{48}$$

where for reasons of thermodynamic stability $(\partial p/\partial \rho_N^0)_T > 0$. Also note that θ^0, expressed in terms of moments of $\bar{\mathscr{N}}$, has an extra minus sign, since $\mathscr{Y} = -\bar{\mathscr{N}}$ and $M_3^0[-\bar{\mathscr{N}}] = -M_3^0[\bar{\mathscr{N}}]$. Hence a *positive* value of θ^0 means a *negative* Gamma state for the particle number distribution and vice versa.

Secondly, unlike in the isothermal-isobaric ensemble, in the grand canonical ensemble there is no general finite value of t for which the moment generating function $\langle e^{t\xi}\rangle$ will diverge. In fact, since $\partial A(N)/\partial N = \mu$, convergence or divergence of the MGF depends on the specific behavior of μ as a function of N. However, for a general Gamma state in the grand canonical ensemble we can rewrite Eq. (33) as

$$\mu(N) = \mu^0 - \frac{N - N^0}{\theta^0(N - N_{\lim})} \tag{49}$$

with

$$N_{\lim} = N^0 - \frac{1}{\theta^0}\left(\frac{\partial N^0}{\partial \mu}\right)_{T,V}. \tag{50}$$

For any physically exact solution $N_{\lim} = N_{\min} = 0$, and hence we can still eliminate one of the parameters, thus reducing the complexity of the solution just like the diverging Gamma state for the volume distribution in the *NpT* ensemble (see the previous section). Eliminating θ^0 from Eq. (50) as $\theta^0 = -(1/N^0)(\partial N^0/\partial \mu)_{T,V}$, we find from Eqs. (31)–(33) the *zero limit Gamma state* expressions

$$\Delta J = N^{0^2}\left(\frac{\partial \mu}{\partial N^0}\right)_{T,V} \ln\left(\frac{N^0}{N}\right), \tag{51}$$

$$N(\mu) = -\frac{N^{0^2}(\partial \mu/\partial N^0)_{T,V}}{\mu - \mu_{\max}}, \tag{52}$$

$$\mu(N) = \mu^0 + N^0\left(\frac{\partial \mu}{\partial N^0}\right)_{T,V}\left[1 - \frac{N^0}{N}\right], \tag{53}$$

with

$$\mu_{\max} = \mu^0 + N^0\left(\frac{\partial \mu}{\partial N^0}\right)_{T,V}, \tag{54}$$

where $\mu_{\max} > \mu^0$ since $(\partial \mu/\partial N^0) > 0$. This formally exact Gamma state could be applicable at every nonzero pressure, and only in the extremely dilute case should be combined with Eq. (8).

Also in this case the most interesting property is the pressure as a function of the density, and we will give a summary of the different statistical states. As the volume is fixed, we can directly find the expressions for Δp, since $\Delta J(\Delta \mu) = -V\Delta p$ and $\Delta \mu$ is a unique and known function of the density for every statistical state.

From Eq. (26) we obtain for the *Gaussian state* G[$\bar{\mathscr{N}}$], using Eq. (46)

$$p = p^0 + \frac{1}{2}\rho_N^0\left(\frac{\partial p}{\partial \rho_N^0}\right)_T\left[\left(\frac{\rho_N}{\rho_N^0}\right)^2 - 1\right] \tag{55}$$

which is equivalent to a second order cumulant expansion of ΔJ in $\beta\Delta\mu$. For a *negative Gamma state* in the number of particles, $\Gamma_-[\bar{\mathscr{N}}]$, where $\theta^0 > 0$ we find from Eq. (31)

$$\begin{aligned}p &= p^0 + \frac{1}{\theta^0}\left[\frac{\rho_{N\,\max}(\rho_N - \rho_N^0)}{\rho_{N\,\max} - \rho_N}\right. \\ &\qquad \left. -(\rho_{N\,\max} - \rho_N^0)\ln\left(\frac{\rho_{N\,\max} - \rho_N^0}{\rho_{N\,\max} - \rho_N}\right)\right], \\ \rho_{N\,\max} &= \rho_N^0\left(1 + \frac{1}{\theta^0(\partial p/\partial \rho_N^0)_T}\right).\end{aligned} \tag{56}$$

TABLE III. Summary of properties of the $p(\rho_N)$ equations in the grand canonical ensemble, for the Gaussian $G[\bar{\mathcal{N}}]$ [Eq. (55)], positive Gamma $\Gamma_+[\bar{\mathcal{N}}]$ [Eq. (56)], zero limit Gamma $\Gamma_+^0[\bar{\mathcal{N}}]$ [Eq. (57)] and negative Gamma state $\Gamma_-[\bar{\mathcal{N}}]$ [Eq. (56)] of the particle number distribution $\rho(\bar{\mathcal{N}})$.

State	θ^0	$\rho_{N\,\min}$	$\lim_{\rho_N\to\rho_{N\,\min}} p$	$\rho_{N\,\max}$	$\lim_{\rho_N\to\rho_{N\,\max}} p$
$G[\bar{\mathcal{N}}]$	0	$-\infty$	∞	∞	∞
$\Gamma_+[\bar{\mathcal{N}}]$	<0	$\rho_N^0\left(1+\frac{1}{\theta^0(\partial p/\partial\rho_N^0)_T}\right)$	$-\infty$[a] [0[a]]	∞	∞
$\Gamma_+^0[\bar{\mathcal{N}}]$	$-\frac{1}{(\partial p/\partial\rho_N^0)_T}$	0	$-\infty$ [0]	∞	∞
$\Gamma_-[\bar{\mathcal{N}}]$	>0	$-\infty$	∞	$\rho_N^0\left(1+\frac{1}{\theta^0(\partial p/\partial\rho_N^0)_T}\right)$	∞[b]

[a]For $\rho_{N\,\min}>0$.
[b]For $\rho_{N\,\max}>0$. Values between square brackets indicate the zero density limits using the exact expression of ΔJ, Eq. (8).

For a *positive Gamma state* in the particle number, $\Gamma_+[\bar{\mathcal{N}}]$, where $\theta^0<0$ we have the same expressions, but we must interpret $\rho_{N\,\max}$ as $\rho_{N\,\min}<\rho_N^0$. Finally, for the *zero limit Gamma state* $\Gamma_+^0[\bar{\mathcal{N}}]$ we find from Eq. (51)

$$p=p^0+\rho_N^0\left(\frac{\partial p}{\partial\rho_N^0}\right)_T\ln\left(\frac{\rho_N}{\rho_N^0}\right). \tag{57}$$

In Table III we have summarized the limit properties of these μVT pressure equations. Clearly, the zero limit Gamma state is the only completely physically correct solution. Note that in all cases where there exist a finite minimum density, i.e., for the $\Gamma_+[\bar{\mathcal{N}}]$ and $\Gamma_+^0[\bar{\mathcal{N}}]$ states, we have to use the complete expression for ΔJ, Eq. (8), in order to obtain the correct zero density pressure limit. Also note that the concept of infinite potential barriers, i.e., hard-sphere-like interactions, is not compatible with positive Gamma states for the number of particles, since for those states the density can reach infinity. In fact, for a system with hard-sphere-like contacts, any exact distribution $\rho(\bar{\mathcal{N}})$ must be defined on the finite interval $[0,\bar{\mathcal{N}}_{\max}]$, which gives rise to extra restrictions on the possible polynomials $P^m(\Delta\bar{\mathcal{N}}^0)$ and $G^n(\Delta\bar{\mathcal{N}}^0)$ in the generalized Pearson system, Eq. (16), and so requires more complex solutions than a Gamma distribution. However, for such systems we can use at least as a local high-density approximation a $\Gamma_-[\bar{\mathcal{N}}]$ state, which has a finite maximum density.

III. THERMODYNAMIC MASTER EQUATIONS AND PHASE TRANSITIONS

In the previous sections of this article and in the preceding article,[7] we derived expressions for various thermodynamic properties as a function of temperature or density, always using the moment generating function evaluated at the reference condition. Expressing the free energy differences in terms of the moment generating function in the actual condition [Eqs. (10), (15) and (83) of the previous article,[7] and Eqs. (2) and (11) of this article] and now combining these with the corresponding thermodynamic relation [Eqs. (18) and (78) of the previous article and Eqs. (3) and (12) of this article] results in a set of closed differential equations (thermodynamic master equations analogous to the one described for the canonical ensemble in previous papers[2,3,6]) with solutions that provide the temperature or the density dependence of the thermodynamic properties. In fact, for a given type of distribution the derivation of the previous sections, where we used the reference moment generating functions, provides such solutions without explicitly solving the corresponding thermodynamic master equation (TME). We can illustrate this using as an example the volume fluctuation distribution in the isothermal-isobaric ensemble. In this case combining Eq. (2) with Eq. (3) we have:

$$V=V+\Delta p\left(\frac{\partial V}{\partial p}\right)_{T,N}+kT\left(\frac{\partial\,\ln\langle e^{\beta\Delta p\Delta\mathcal{V}}\rangle}{\partial p}\right)_{T,N}, \tag{58}$$

whence

$$\Delta p\left(\frac{\partial V}{\partial p}\right)_{T,N}=-kT\left(\frac{\partial\,\ln\langle e^{\beta\Delta p\Delta\mathcal{V}}\rangle}{\partial p}\right)_{T,N}, \tag{59}$$

where, as we showed, the central moment generating function $G_{\Delta\mathcal{V}}(\beta\Delta p)=\langle e^{\beta\Delta p\Delta\mathcal{V}}\rangle$ can be expressed in terms of a set of volume derivatives with respect to the pressure. Hence Eq. (59) is a closed ordinary differential equation and must have a unique solution providing $V(p)$ at a given temperature and number of particles. Moreover, since the type of differential equation in Eq. (59) is fully defined by the type of volume distribution at one arbitrary pressure p, it follows that the type of distribution must be conserved at every other pressure. It should then be clear that the expression of $V(p)$ obtained in the previous sections, directly differentiating the logarithm of the central moment generating function at the reference condition with respect to p [using Eq. (1) in Eq. (3)], must be the solution of Eq. (59), as it follows from the fact that Eq. (59) has a unique solution defined by one type of distribution or moment generating function. The same argument can be easily applied to any possible fluctuation-ensemble combination, leading exactly to the same result.

As previously noted for the potential energy fluctuation in the canonical ensemble, this fact has very important consequences, implying, for instance, that the knowledge at one

arbitrary pressure of the exact volume distribution contains complete information on the volume fluctuations at every other pressure and hence the knowledge at this single point provides the full thermodynamics at every other possible pressure for a given temperature and number of particles. Only the presence of a singularity in a TME can restrict the range of applicability of its solution, implying in general the existence of two independent branches of the solution at the two sides of the singularity. From a general thermodynamic point of view this seems to be the case when a system undergoes a phase transition where many of its properties are considered to have a singularity. However, with the use of statistical mechanics we can understand that this common thermodynamic consideration on phase transitions must be regarded only as a very useful approximation, but never really exact.[25] In fact, in order to have real singularities at the phase transition we should assume that the system is exactly confined in one region of the available phase space and then, at the phase transition, moves into another exactly confined part corresponding to the new condition. In this case the moments of the distribution and hence the thermodynamic properties can have a real singularity. It is easy to see that this is impossible because any exact confinement can only be produced by infinite energy barriers in phase space, which are of course noncompatible with any transition (the system would remain trapped in the initial region at every temperature and density). More in general, if a set of moments are diverging at a certain temperature they will still diverge at any higher temperature, implying that a real singularity for the moments at a single finite temperature should be impossible. In a real system even when it is in a stable monophasic condition there is always a nonzero probability, although numerically virtually zero, that the system is in the multiphase phase-space region, hence having a phase separation or vice versa when the system is in a stable multiphase condition. The definition of a stable monophasic or multiphasic condition can only be based on probability. Hence the information which is in principle available at one state point could be really enough to rebuild the thermodynamic behavior at any other state point and therefore for each TME a single solution with no singularities should be always expected.

Clearly in usual monophasic conditions a system can be described virtually exactly as really confined in the single phase phase-space region, since the probability for any transition outside this region is almost zero, and therefore the corresponding distributions (for the energy, volume and number of particles) are virtually indistinguishable from those obtained for an exactly confined system. However, such usually negligible ''hidden'' information will become essential, influencing the whole shape of the distributions and not only the very far tails, when the system is close to the critical point where large microscopic fluctuations are possible, and at the coexistence line where a system becomes macroscopically multiphasic. In the latter case the transition is very sharp in temperature or density and corresponds to a catastrophic exchange of probability between the monophasic and multiphasic phase-space regions. Phase transitions can therefore be usefully modelled as thermodynamic discontinuities although no mathematical singularities really occur. In practice the exact TME solutions although existing, are extremely difficult to be properly modeled. We showed[6] that the statistical states necessary to describe a multiphasic system are much more complex than the ones which can be used successfully for single phase conditions. Hence, since any exact solution of a TME should describe both the monophasic as well the multiphasic condition, its complexity[6] should be at least the same as that of the simplest statistical state needed to model the multiphase system. Such highly complex unimodal distributions (defined by a large number of moments or derivatives) are really necessary to reproduce the very irregular behavior of a system at phase transitions or at the critical point. In the latter case the extra complication of the correlation length which tends to infinity could even imply that locally the distribution is not necessarily properly modeled by an exact unimodal curve. It is clear then that statistical states which can reproduce with high accuracy only the thermodynamics of monophasic systems must be always regarded as excellent approximations in a monophasic range of the exact statistical state, unable to describe directly any multiphase condition.

IV. RESULTS

First we derive for an ideal gas the volume distribution in the *NpT* ensemble and the particle number distribution in the μVT ensemble. For simplicity we will give a description for monatomic molecules, since the generalization to polyatomic molecules is straightforward and does not alter the results.

In the *isothermal-isobaric ensemble* we obtain from the monatomic ideal gas partition function[25]

$$\Delta_{\mathrm{id}}=\frac{(q^e)^N\Lambda^{-3N}}{v(\beta p)^{N+1}} \tag{60}$$

and Eq. (2)

$$\Delta G=kT\ \ln\ G_{\mathscr{V}}(\beta\Delta p)=kT\ \ln\frac{\Delta^0_{\mathrm{id}}}{\Delta_{\mathrm{id}}}=kT\ \ln\left(\frac{\beta p}{\beta p^0}\right)^{N+1}. \tag{61}$$

Hence, with $t=\beta\Delta p$ we have

$$G_{\mathscr{V}}(t)=\left(\frac{\beta p}{\beta p-t}\right)^{N+1} \tag{62}$$

and using the general relation $G_{\Delta\mathscr{X}}(t)=e^{-tX}G_{\mathscr{X}}(t)$, we find

$$G_{\Delta\mathscr{V}}(t)=e^{-tV}\left(\frac{\beta p}{\beta p-t}\right)^{N+1}. \tag{63}$$

For a Gamma distribution $\rho(\xi)$ the MGF [see Eq. (30)] is a similar expression

$$G_{\Delta\xi}(t)=e^{-t(b_0/b_1)}\left(\frac{1/b_1}{1/b_1-t}\right)^{b_0/b_1{}^2} \tag{64}$$

and moreover, since for an ideal gas[26] $V=(N+1)kT/p$, $\partial V/\partial p=-(N+1)kT/p^2$ and $\partial^2V/\partial p^2=2(N+1)kT/p^3$, we obtain with $b_0=M_2$, $b_1=M_3/(2M_2)$ and Eq. (17)

$$\frac{1}{b_1}=\beta p;\quad \frac{b_0}{b_1}=V;\quad \frac{b_0}{b_1{}^2}=N+1, \tag{65}$$

which proves that the volume distribution of an ideal gas in the isothermal-isobaric ensemble is a diverging Gamma distribution ($b_1=1/\beta p$), and also suggests that it might be a good description for real gases as well.

Note that since for an ideal gas the volume and the internal energy are uncorrelated,[21] the MGF of the instantaneous enthalpy distribution function in the *NpT* ensemble is the product of $G_{\mathscr{U}}(t)$ and $G_{p\mathscr{V}}(t)$, where $G_{\mathscr{U}}(t)=(\beta/\beta-t)^{3N/2}$ follows from the distribution of the kinetic energy of a monatomic gas with $3N$ degrees of freedom[7] and $G_{p\mathscr{V}}(t)=G_{\mathscr{V}}(pt)$, so

$$\begin{aligned} G_{\mathscr{H}}(t) &= G_{\mathscr{U}+p\mathscr{V}}(t) \\ &= G_{\mathscr{U}}(t)\cdot G_{p\mathscr{V}}(t) \\ &= \left(\frac{\beta}{\beta-t}\right)^{(3/2)N}\left(\frac{p\beta}{p\beta-pt}\right)^{N+1}=\left(\frac{\beta}{\beta-t}\right)^{(5/2)N+1} \end{aligned} \tag{66}$$

which is in agreement with Eq. (103) of the preceding article.[7]

For a monatomic ideal gas in the *grand canonical ensemble* the partition function is given by[25]

$$\Xi_{\mathrm{id}}=\sum_{\mathscr{N}=0}^{\infty}\frac{1}{\mathscr{N}!}(e^{\beta\mu}q^e q^{\mathrm{kin}}V)^{\mathscr{N}}=\exp\{e^{\beta\mu}q^e q^{\mathrm{kin}}V\}. \tag{67}$$

Hence the discrete probability distribution is

$$\rho(\mathscr{N})=\frac{(e^{\beta\mu}q^e q^{\mathrm{kin}}V)^{\mathscr{N}}}{\mathscr{N}!\,\Xi_{\mathrm{id}}}=\frac{a^{\mathscr{N}}e^{-a}}{\mathscr{N}!}, \tag{68}$$

which is a Poisson distribution[8,9] with $a=e^{\beta\mu}q^e q^{\mathrm{kin}}V=\langle\mathscr{N}\rangle=N$. Rearranging this expression gives the usual expression for the chemical potential of a classical ideal gas,[25] $\mu_{\mathrm{id}}=-kT\ln(q^e q^{\mathrm{kin}}V/N)$. Obviously, since V is fixed also $\rho(\rho_N)$ is a Poisson distribution. Using the fact that the moment generating function of this Poisson distribution is given by[8]

$$G_{\mathscr{N}}(t)=\langle e^{t\mathscr{N}}\rangle=\exp\{a(e^t-1)\} \tag{69}$$

and combined with Eq. (4),

$$-\Delta J=V\Delta p=kT\ln\langle e^{\beta\Delta\mu\mathscr{N}}\rangle_{\mu^0}=kT\ln G^0_{\mathscr{N}}(\beta\Delta\mu) \tag{70}$$

we correctly find

$$\rho_N(\mu)=\rho_N^0 e^{\beta\Delta\mu}, \tag{71}$$

$$\mu=\mu^0+kT\ln\left(\frac{\rho_N}{\rho_N^0}\right), \tag{72}$$

$$p(\rho_N)=p(\rho_N^0)+kT(\rho_N-\rho_N^0). \tag{73}$$

While in the isothermal-isobaric ensemble the Gamma state for the volume is the exact statistical state of an ideal gas, a Gamma state for the density in the grand canonical ensemble is not, and can only be an approximation to this ideal gas Poisson state. Or, in other words, a diverging Gamma state for the volume $\Gamma_+^d[\mathscr{V}]$ might in general be a good description at least of the gas phase, whereas a zero-limit Gamma state for the number of particles $\Gamma_+^0[\bar{\mathscr{N}}]$, although physically acceptable, will never be a good description, as not even the ideal gas behavior is properly described.

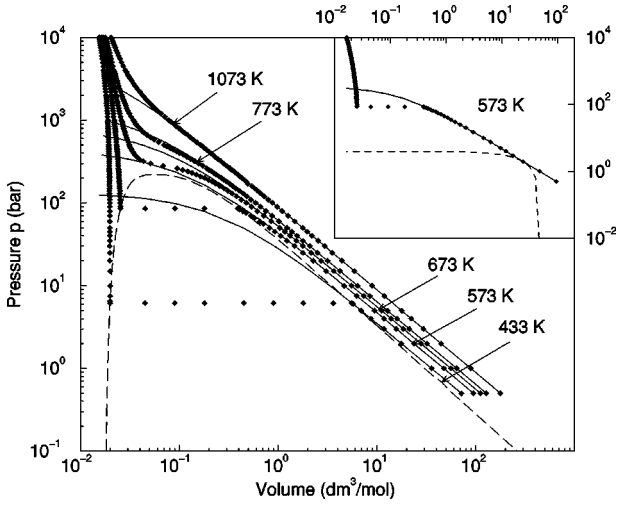

FIG. 1. Pressure p of water along different isotherms. Legend: experimental values (♦) and diverging Gamma state $\Gamma_+^d[\mathscr{V}]$, Eq. (45) (——). The coexistence line is indicated by a long dashed line. Note the double logarithmic scale. The critical temperature is 647.3 K (Ref. 27). Insert: comparison of Gaussian, Eq. (43) (— — —) and diverging Gamma (——) at 573 K.

Based on this we tried to model the p-V relation of gaseous water using a diverging Gamma state in the volume, $\Gamma_+^d[\mathscr{V}]$, Eq. (45). Experimental data were again taken from Schmidt.[27] For various isotherms (433, 573, 673, 773 and 1073 K) we obtained input data of p^0 and V^0 at low pressure ($p^0=2.0$ bar), giving slightly negative values of $V_{\min}$ ($V_{\min}=-0.27$, -0.11, -0.07, -0.05 and -0.01 dm^3/mol with increasing temperature). Of course, at high temperature $V_{\min}\to 0$ as should be for an ideal gas. Results are given in Fig. 1. For isotherms below the critical temperature ($T_c=647.3$ K) the predictions are correct almost up to the coexistence line, and the highest isotherm (1073 K) shows correct predictions up to the critical volume (0.0571 dm^3/mol), see also Fig. 3. For smaller volume (larger density) a simple diverging Gamma state is not able to accurately describe the pressure any more. For comparison we also present a second order cumulant expansion of the free energy difference in $\beta\Delta p$, equivalent to a Gaussian state, Eq. (43). Results for one isotherm (573 K) are given in the insert of Fig. 1 (the other isotherms give similar results). Although a Gaussian state uses more input data than a diverging Gamma state, the behavior of the former is clearly wrong. Just as for the temperature dependence,[7] the use of a physically acceptable Gamma distribution increases the quality of the model considerably, compared to a simple cumulant expansion.

For the dense part of the phase diagram we tried as a local approximation a negative Gamma state in the number of particles, $\Gamma_-[\bar{\mathscr{N}}]$, Eq. (56), for the different isotherms, see Fig. 2. Although it is a local approximation, we expect it to be better at high density than the physically acceptable zero limit Gamma state, since the former has a maximum density $\rho_{N\,\max}$, where a singularity occurs in accordance to the usual simple ''hard sphere'' model of liquids. For each

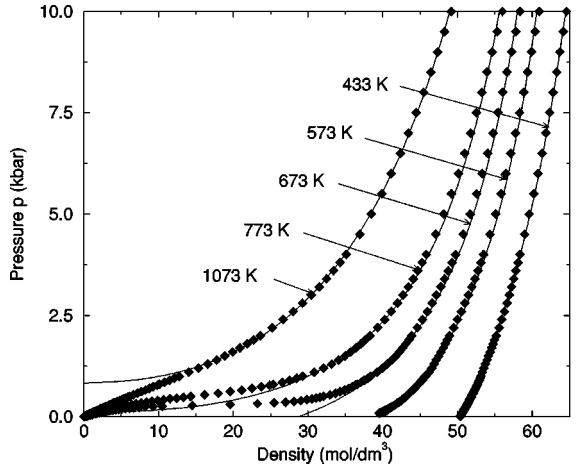

FIG. 2. Pressure p of water along different isotherms. Legend: experimental values (♦) and negative Gamma state $\Gamma_-[\bar{\mathcal{N}}]$, Eq. (56) (——).

isotherm initial values were obtained in a single point within the range $1200<p^0<3400$ bar, $30.4<\rho_N^0<57.5$ mol/dm^3, $0.03<\theta^0<0.08$ (kJ/mol)$^{-1}$ and $72<\rho_{N\,\max}<88$ mol/dm^3. The latter corresponds to a hard-sphere radius $1.49<r_{\mathrm{HS}}<1.60$ Å, which is clearly larger than the value $r_{\mathrm{HS}}\cong 1.35$ Å previously obtained from the phase-space confinement ϵ along isochores.[6] From Fig. 2 it is clear that a $\Gamma_-[\bar{\mathcal{N}}]$ state is perfectly able to describe the pressure of a dense liquid like water; up to the coexistence line for isotherms below T_c (see also Fig. 3) and for the highest isotherm up to the critical density (17.51 mol/dm^3). Note that also in this case a second order cumulant expansion (equivalent to a Gaussian state) is much worse than the used Gamma state (data not shown).

In Fig. 3 we present predictions from both the $\Gamma_+^d[\mathcal{V}]$ and the $\Gamma_-[\bar{\mathcal{N}}]$ states in the vicinity of the critical point. For isotherms below T_c the gas side is properly described by a $\Gamma_+^d[\mathcal{V}]$ state and the liquid side by a $\Gamma_-[\bar{\mathcal{N}}]$ state. At 1073 K we see that both solutions meet at about the critical volume. For intermediate temperatures there is a region around the critical point which cannot be accurately described by either one of the statistical states: the complexity of the model distributions are too low in this part of the phase diagram.

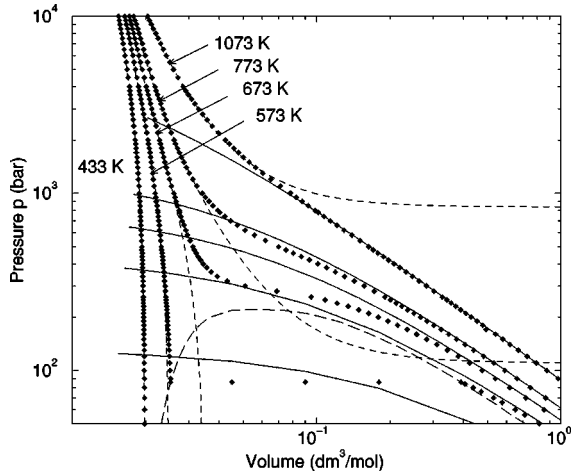

FIG. 3. Pressure p of water along different isotherms, focusing on the critical point area. Legend: experimental values (♦), diverging volume Gamma state of Fig. 1 (——) and negative particle number Gamma state of Fig. 2 (— — —).

V. CONCLUSION

In this article we showed how to extend the quasi-Gaussian entropy theory in an exact way to describe density dependence of thermodynamic properties in noncanonical ensembles using the probability distribution of the volume and number of particles. We derived general expressions for the solutions of thermodynamic master equations for the density dependence in the NpT and μVT ensemble, and described specific aspects of these conditions. General Gaussian and Gamma statistical states were derived, as well as special Gamma states, such as the diverging Gamma (NpT) and zero limit Gamma state (μVT), according to the specific physical constraints of each ensemble. These Gaussian and Gamma states were used to reproduce the thermodynamics of water in gas and liquid conditions. In contrast to the situation in the canonical ensemble using the energy fluctuations, in these noncanonical ensembles we encounter phase transitions. Following the usual thermodynamic approach (i.e., regarding the phase transitions as singularities), we have two distinct solutions for the subcritical isotherms: a gas and a liquid one.

In this article we first showed that in the NpT ensemble an ideal gas is described by a diverging Gamma state for the volume fluctuations, suggesting that in general such a diverging Gamma state could be a good description, at least of the gas behavior. In the case of the grand canonical ensemble, on the contrary, the ideal gas statistical state for the particle number fluctuations is given by a (discrete) Poisson distribution, implying that even the physically acceptable zero limit Gamma state is not able to reproduce exactly the ideal gas behavior. This suggests that Gamma states for the particle number fluctuations are likely to be useful especially as high-density local descriptions (negative Gamma states with a maximum density) but are not accurate in describing the gas range density dependence.

Secondly, as previously obtained for the temperature dependence,[7] also for the density dependence a considerable part of the (fluid) phase diagram can be described by Gamma states and only at the phase transitions or in the vicinity of the critical point more sophisticated statistical states are required. The results clearly show that we can describe the thermodynamics of water using two Gamma state solutions, a low-density (gas) diverging Gamma state for the volume fluctuations, and a high-density (liquid) diverging Gamma state for the particle number fluctuations, but no single Gamma state can be used as a unique statistical state of the system for all densities, even at supercritical isotherms. This implies that for a real system its unique exact solution, able to describe both gas and liquid conditions including phase transitions and the critical point region, is beyond the Gamma level of the theory in NpT and μVT ensembles.

Interestingly, while for the temperature dependence[7] at least for water both the liquid and the gas side can be accu-

rately modeled by gamma states for the enthalpy fluctuations in the *NpT* ensemble, in the case of the density dependence, we can only describe the liquid and gas behavior using two gamma states from different ensembles: a volume *NpT* diverging gamma state on the gas side and a particle number μVT negative gamma state for the liquid side. As obtained for the temperature dependence in the previous paper, also for the density dependence a second order cumulant expansion is much worse than the used gamma states.

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